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Changes in the Key Odorants of Italian Hazelnuts (*Coryllus avellana* L. Var. Tonda Romana) Induced by Roasting

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Application of a comparative aroma extract dilution analysis on aroma distillates isolated from either raw Italian hazelnuts or a roasted hazelnut material produced thereof revealed 37 odor-active compounds in the raw nuts, whereas 46 aroma compounds were detected in the roasted nut material. 2-Methoxy-3-isopropylpyrazine and 2-methoxy-3,5-dimethylpyrazine as well as 5-methyl-4-heptanone predominated with the highest flavor dilution factors in the raw nuts, whereas 2-acetyl-1-pyrroline, 2-propionyl-1-pyrroline, 2-furfurylthiol, and 2-thenylthiol as well as (*Z*)-2-octenal, (*Z*)-2-nonenal, and (*Z*)-2-decenal showed the highest odor activities in the roasted nuts. These odorants, as well as several others, were previously unknown in hazelnuts. In addition, the intensely seasoning-like smelling 3,5,5′-trimethyl-2(5*H*)-furanone was identified for the first time as a food aroma compound on the basis of a newly developed synthetic route and NMR measurements.

KEYWORDS: Hazelnut aroma; filberts; 2-thenylthiol; 5-methyl-4-heptanone; 3,5,5′-trimethyl-2(5*H*)-furanone

INTRODUCTION

The fruits of the hazelnut tree (*Corylus avellana*), known as hazelnuts or filbert nuts, have been used since ancient times as a valuable source of nutrients, such as essential fatty acids or vitamins. Today, the yearly production of hazelnuts is ∼900 000 t, with Turkey being the major supplier, followed by Italy and the United States (http://www.fao.org/corp/statistics/eu). A minor part of the nut crop is consumed as such, that is, in cakes, whereas the major part of the harvest undergoes a roasting process and is finally used, for example, in confectionery or as the main ingredient in cocoa/hazelnut spreads. Because raw hazelnuts have a rather bland aroma, it can be assumed that the odorants responsible for the characteristic hazelnut smell are generated by the roasting procedure from odorless precursors present in the raw nut.

However, although the typical aroma of roasted hazelnuts is appreciated all over the world, the volatile fraction of roasted nuts has been the subject of only a few studies so far. Kinlin et al. (*1*) performed the first comprehensive study on the volatiles of Oregon hazelnuts, and these authors have been able to identify 228 compounds in nut extracts isolated by different distillation techniques. Emberger (*2*) analyzed the volatiles present in raw hazelnuts and reported 5-methyl-(*E*)-2-hepten-4-one for the first time as a food constituent. Because this compound was found to elicit a hazelnut-like aroma at the low odor threshold of 0.05 μg/L in water, it was suggested to be one of the character impact odorants of hazelnuts and has been referred to as "filbertone" in the scientific literature since then. Silberzahn (*3*) confirmed the presence of 5-methyl-(*E*)-2-hepten-4-one and reported on another 142 volatiles in raw hazelnuts. The unsaturated ketone may occur in four isomeric forms; meanwhile, analytical methods to separate all isomers (*4*, *5*) as well as data on their odor thresholds are available (*4*). All four isomers have already been found in roasted hazelnuts, and the composition of the isomers suggested that a thermal generation might occur in addition to their biochemical formation in the raw nuts.

Langourieux et al. (*6*) were the first to apply GC−olfactometry and CHARM analysis on an extract obtained from roasted Italian hazelnuts. However, only four compounds, namely, 2- and 3-methylbutanal, 5-methyl-(*E*)-2-hepten-4-one, 2-methyl-3-furanthiol, and an unknown compound with a butter-like odor were detected with high odor intensities. Quantitative measurements performed on a very few compounds showed that, in particular, 3-methylbutanal and 2-methyl-3-furanthiol increased as a function of roasting time (*6*).

Alasalvar et al. (*7*) compared the changes in the concentrations of ∼60 volatiles during roasting of Turkish hazelnuts. Most volatiles were much increased during roasting, that is, methylpropanal, 2- and 3-methylbutanal, toluene, 1-cyclopentylethanone, 1,2,4-trimethylbenzene, 5-methyl-(*E*)-2-hepten-4-one, and several pyrazines. However, although the overall sensory evaluation of the roasted hazelnuts revealed an increase in burnt, roasty, or coffee- and chocolate-like odors in the roasted as compared to the raw nuts, in this study no attempts were undertaken to correlate the odor contribution of single volatiles to the overall aroma.

The literature data suggest that the overall odor of roasted hazelnuts is evoked by a set of aroma compounds either biochemically generated during ripening of the nuts (*2*−*4*) or generated by a thermal conversion of odorless precursors during roasting, for example, 3-methylbutanal (*6*, *7*) from a Strecker degradation of leucine. However, to date, no data on the key odorants in raw hazelnuts obtained by combining analytical and

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sensory methods are available. Furthermore, although quantitative changes in several hazelnut volatiles caused by roasting have been reported, the importance of these changes for the overall aroma is still open.

An aroma extract dilution analysis (AEDA) allows one to select the most odor-active compounds from the bulk of odorless volatiles present in distillates of food volatiles (*8*). As recently shown for peanuts (*9*) and cocoa beans (*10*), application of a comparative AEDA (*8*) on isolates from the same amount and the same batch of raw and processed material, changes in the flavor dilution (FD) factors give clear hints on aroma compounds formed from odorless precursors during roasting, but the method also identifies the key odorants already present in the raw material.

Because studies aimed at clarifying the key odorants in raw as well as in roasted hazelnut material were scarcely performed, the purpose of the present study was to characterize the key odorants in the same batch of raw and roasted Italian hazelnuts by application of the AEDA followed by identification experiments, in order to get insights into aroma formation during roasting of hazelnuts on a molecular basis.

MATERIALS AND METHODS

Hazelnuts. Hazelnuts of the variety "Tonda Romana" were obtained from the trade (Seeberger, Ulm, Germany). The company guaranteed continuous supply from the same producer. New hazelnut batches were used for every workup procedure.

Chemicals. *Reference Odorants*. The reference compounds were supplied by the companies listed in parentheses: 3-*sec*-butyl-2-methoxypyrazine, ethyl 2-methylbutanoate, hexanal, 2-methoxy-3-isobutylpyrazine, 2-methoxy-3-isopropylpyrazine, linalool, 4-methylphenol (*p*-cresol), 3-(methylthio)propanal (methional), (*E*,*E*)-2,4-nonadienal, (*E*)-2-nonenal, octanal, ethyl propanoate, α-pinene, 2,3-butandione, 2,3-pentandione, dimethyl trisulfide, nonanal, 2,3,5-trimethylpyrazine, 2-furfurylthiol, (*E*)-2-octenal, 2-ethyl-3,5-dimethylpyrazine, (*E*,*Z*)-2,6-nonadienal, phenylacetaldehyde, 2- and 3-methylbutanoic acid, (*E*,*Z*)-2,4-nonadienal, (*E*,*Z*)-2,4-decadienal, γ-heptalactone, (*E*,*E*)-2,4-decadienal, γ-octalactone, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, and γ-nonalactone (Aldrich, Steinheim, Germany); 3-methylbutanal (Fluka, Buchs, Switzerland); (*E*)-2-decenal (Lancaster, Mühlheim/Main, Germany); acetic acid, 2-methylbutanal, butanoic acid, 2-phenylethanol, 4-methoxybenzaldehyde (Merck, Darmstadt, Germany); 2-thenylthiol (Acros, Geel, Belgium); 1-octen-3-one and (*Z*)-2-decenal (Lancaster, Ward Hill, MA); and 2-methoxyphenol (Serva, Heidelberg, Germany). (*E*)-β-Damascenone and (*Z*)-heptenal were kindly provided by Symrise (Holzminden, Germany).

The following compounds were synthesized as reported in the literature: 2-acetyl-1-pyrroline (*11*), 2,4,6-nonatrienal (*12*), 2-propionyl-1-pyrroline (*13*), *trans*-4,5-(*E*)-2-decenal (*14*), and (*Z*)-2-nonenal (*15*). (*Z*)-2-Octenal was isolated from (*E*)-2-octenal as reported previously for (*E*,*Z*)-2,4-decadienal (*14*).

Chemicals. 1-Butyne-3-ol and 3-methyl-2-pentanone were obtained from Aldrich, and bromine, lithium hydroxide, palladium on active charcoal, and silica gel 60 were obtained from Fluka. 2-Bromobutane, cyanuric acid, dichloromethane, diethyl ether (anhydrous), 2,6-dimethylpyrazine, Na_2SO_4 (anhydrous), iodine, magnesium, methanol (anhydrous), pentane (anhydrous), orthophosphoric acid (85%), phosporus tribromide, sodium carbonate, sodium hydrogencarbonate, sodium methylate, sodium sulfite (anhydrous), and sulfuric acid were obtained from Merck; Dess−Martin periodinane (1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3-(1*H*)-one) was obtained from Lancaster and dichloromethane (anhydrous) from Riedel-de-Haen (Seelze, Germany).

Syntheses. *3,5,5-Trimethyl-2(5H)-furanone*. The odorant was prepared in a three-step synthesis (**Figure 1**) as detailed below.

(*a*) *4-Hydroxy-2,4-dimethyl-(Z)-2-pentenol*. Magnesium (0.75 g; small pieces) was covered with anhydrous diethyl ether (20 mL), and methyl iodide (4.35 g), dissolved in anhydrous diethyl ether (10 mL), was slowly added within 30 min at 0 °C. Then, 3-methyl-2(5*H*)-furanone (1 g) dissolved in anhydrous diethyl ether (10 mL) was added, and the reaction mixture was refluxed for 2 h. After cooling, diethyl ether (100 mL) was added, and the mixture was poured onto crushed ice (50 g). The white precipitate formed was dissolved using a saturated aqueous ammonium chloride solution (∼100 mL). The aqueous phase was extracted twice with diethyl ether (total volume = 200 mL), and the combined organic layer was dried over anhydrous Na_2SO_4 and finally concentrated to ∼5 mL. During concentration, the solvent was stepwise exchanged by the addition of dichloromethane.

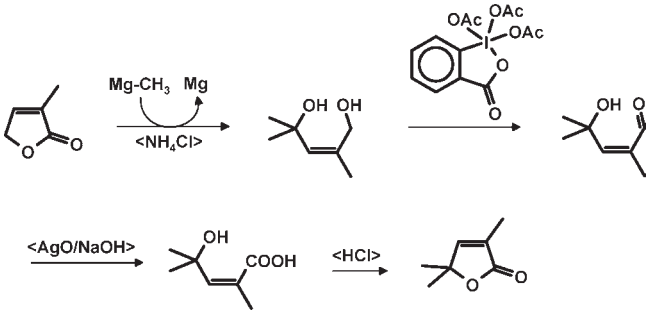

Figure 1. Synthetic route used in the preparation of 3,5,5′-trimethyl-2(5*H*)-furanone.

(*b*) *4-Hydroxy-2,4-dimethyl-(Z)-2-pentenal*. 4-Hydroxy-2,4-dimethyl-(*Z*)-2-pentenol dissolved in anhydrous dichloromethane (20 mL) was slowly added within 10 min to a suspension of Dess−Martin periodinane (3.23 g; 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one) in anhydrous dichloromethane (80 mL). The mixture was stirred for 1 h at room temperature, then diethyl ether (200 mL) was added, and the organic layer was extracted with aqueous sodium thiosulfate (200 mL; 1 mol/L). This procedure was repeated twice. Finally, the organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated to ∼5 mL.

(*c*) *4-Hydroxy-2,4-dimethyl-(Z)-2-pentenoic Acid Lactone*. Silver(I) oxide (1.8 g) was suspended in distilled water (10 mL) kept at 0 °C. Sodium hydroxide (0.4 g) dissolved in distilled water (20 mL), followed by 4-hydroxy-2,4-dimethyl-(*Z*)-2-pentenal, was added, and the mixture was stirred in an ice bath for 18 h. The silver catalyst was filtered off and, to form the respective lactone, the filtrate was adjusted to pH 2 with hydrochloric acid (2 mol/L; 50 mL) and stirred for another 10 min. The aqueous layer was extracted twice with diethyl ether (total volume = 200 mL), and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to ∼1 mL.

MS-EI: *m*/*z* (%) 126 (5), 111 (100), 83 (90), 68 (25), 55 (10), 43 (95). MS-CI: *m*/*z* (%) 127 (100).

The following proton magnetic resonance spectrum (^{1}H NMR) was obtained in deuterated diethyl ether (TMS standard): doublet at δ 1.45 ($J_{4,7,7'}$ = 2.9 Hz), doublet at δ 2.03 ($J_{4,6}$ = 2.9 Hz), and a multiplet at δ 7.1−7.2 (H at C4).

2,6-Dimethyl-3-methoxypyrazine. The synthesis was performed following the procedure reported in ref (*16*) with some modifications. To a solution of lithium hydroxide (0.6 g) and cyanuric acid (1.6 g), dissolved in distilled water (125 mL), was added bromine (4 g), and the mixture was gently shaken until the bromine was dissolved. The mixture was stored for 24 h at −18 °C with occasional shaking. The dibromocyanuric acid formed was filtered off and washed with ice-cold water (20 mL). The product was freeze-dried to remove the residual water. 2,6-Dimethylpyrazine (1.6 g) was dissolved in H_2SO_4 (10%; 10 mL), and the dibromocyanuric acid, dissolved in H_2SO_4 (10%; 24 mL), was slowly dropped into the mixture with stirring. The solution was left for 45 min at room temperature, then poured on ice (50 g), and extracted twice with dichloromethane (200 mL total volume). The organic layer was washed with distilled water (100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed by means of a rotary evaporator, and the 2-bromo-3,5-dimethylpyrazine formed was dissolved in dry methanol (4 mL). Sodium methylate (2 g), dissolved in methanol (2 mL) was added, and the whole mixture was refluxed for 2 h. After cooling, distilled water (50 mL) was added, and the mixture was extracted twice with diethyl ether (total volume = 200 mL). The organic layer was dried over anhydrous Na_2SO_4, and the 2-methoxy-3,5-dimethylpyrazine obtained was isolated by silica gel column

chromatography using pentane/diethyl ether mixtures of increasing polarity (90:10, 85:15, 75:25, 50:50, 0:100, v/v). The pyrazine was detected by GC-MS in the third fraction.

MS-EI: *m*/*z* (%) 42 (25), 54 (25), 68 (15), 82 (25), 95 (20), 109 (45), 120 (30), 138 (100). MS-CI: *m*/*z* (%) 139 (100).

5-Methyl-4-heptanone. The compound was prepared in a three-step synthesis by a Grignard reaction of 2-brombutane with butanal followed by oxidation as detailed below.

(*a*) *2-Bromobutane*. 2-Butanol dissolved in anhydrous diethyl ether (30 mL) was slowly dropped into phosphorus tribromide (5 mL) under an atmosphere of pure nitrogen while the mixture was kept below 5 °C. After stirring at 22 °C for 24 h, the solution was poured onto crushed ice (50 g) and extracted twice with diethyl ether (total volume = 200 mL). The combined organic layers were washed with aqueous sodium carbonate solution (0.5 mol/L; 100 mL), dried over anhydrous Na_2SO_4, and concentrated to ∼2 mL.

(*b*) *3-Methyl-4-heptanol*. Magnesium (2 g; fine pieces) kept at 0 °C in an ice bath was suspended in anhydrous diethyl ether (∼5 mL), and 2-bromobutane dissolved in anhydrous diethyl ether (2 mL) was slowly added. Some crystals of iodine were used to start the reaction, and the mixture was stirred at 0 °C for 30 min. Then, butanal (1.6 g) dissolved in anhydrous diethyl ether (5 mL) was added, and the mixture was refluxed for 2 h. After cooling, crushed ice (50 g) was added, and a few droplets of hydrochloric acid (2 mol/L) were used to dissolve the precipitate formed. The aqueous solution was extracted twice with diethyl ether (total volume = 200 mL), and the combined organic layers were washed with aqueous saturated sodium sulfite (100 mL), followed by aqueous saturated sodium carbonate (100 mL) and, finally, distilled water (100 mL). The solution was dried over anhydrous Na_2SO_4 and concentrated to ∼5 mL.

(*c*) *5-Methyl-4-heptanone*. A solution of Dess−Martin periodinane (5 g; 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one) dissolved in anhydrous dichloromethane (80 mL) was slowly added to a solution of the 3-methyl-4-heptanol in anhydrous dichloromethane (40 mL) within 10 min. After 60 min of stirring, diethyl ether (200 mL) was added, and the organic phase was extracted with aqueous sodium thiosulfate (200 mL, 1 mol/L). The extraction procedure was repeated twice, and the organic layer was washed with aqueous saturated sodium hydrogencarbonate (200 mL) followed by brine, dried over anhydrous Na_2SO_4, and concentrated to ∼5 mL. The 5-methyl-4-heptanone formed was purified by silica gel column chromatography.

MS-EI: *m*/*z* (%) 57 (100), 71 (80), 85 (35), 100 (35), 128 (50). MS-CI: *m*/*z* (%) 129 (100).

The following proton magnetic resonance spectrum (^{1}H NMR) was recorded in deuterated diethyl ether: triplet at δ 0.85 (H1, $J_{1,2}$ = 7.45 Hz), triplet at δ 0.90 (H7, $J_{6,7}$ = 7.4 Hz), doublet at δ 1.05 (H8, $J_{5,8}$ = 6.95 Hz), multiplet at δ 1.35 (H2, $J_{1,2}$ = 7.45 Hz, $J_{2,3}$ = 6.7 Hz), quartet at δ 1.60 (H6 and 1), multiplet at δ 1.65 (H6 and 2), triplet at δ 2.40 (H3), multiplet at δ 2.45 (H5).

5-Methyl-(E)-2-hepten-4-one. 3-Methyl-2-pentanone (6.25 g) was acidified with concentrated sulfuric acid (∼0.5 mL), and the solution was kept at 45 °C until a red-brown color was formed. Acetaldehyde in dry diethyl ether (2 mL) was dropped into the solution in three portions with stirring, and this was continued for another 30 min. After cooling, aqueous sodium carbonate (20 mL; 0.5 mol/L) was used to alkalize the solution. The mixture was extracted twice with diethyl ether (total volume = 200 mL), dried over anhydrous Na_2SO_4, and concentrated to ∼10 mL by means of a Vigreux column.

The 5-methyl-2-hydroxy-4-heptanone formed and orthophosphoric acid (85%; 1 g) were combined and slowly heated to 70 °C. While the residual diethyl ether was distilled off, the mixture was heated to ∼110 °C and kept for 10 min. After cooling, aqueous sodium bicarbonate (about 20 mL; 0.5 mol/L) was added, and the aqueous layer was extracted twice with diethyl ether (total volume = 200 mL), dried over anhydrous Na_2SO_4, and concentrated to ∼5 mL on a Vigreux column. The 5-methyl-(*E*)-2-hepten-4-one formed was purified by silica gel chromatography using pentane/diethyl ether mixtures (100:0, 95:5, 90:10, 85:15, 50:50, 0:100, v/v). The target compound was identified in fractions 2 and 3.

MS-EI: *m*/*z* (%) 69 (100), 98 (15), 111 (12), 126 (1). MS-CI: *m*/*z* (%) 127 (100).

The following proton magnetic resonance spectrum (^{1}H NMR) was monitored in deuterated diethyl ether: triplet at δ 0.9 (H7, $J_{6,7}$ = 7.45 Hz), doublet at δ 1.07 (H8, $J_{5,8}$ = 6.97 Hz), multiplet at δ 1.4 (H61, $J_{5,6}$ = 6.8 Hz, $J_{6,7}$ = 7.45 Hz), multiplet at δ 1.7 (H62, $J_{5,6}$ = 6.8 Hz, $J_{6,7}$ = 7.45 Hz), singlet at δ 2.12 (H1), sextet at δ 2.45 (H5, $J_{5,8}$ = $J_{5,6}$ = 6.8 Hz).

Isolation of the Hazelnut Volatiles; Roasting Conditions. Raw hazelnuts (200 g) were frozen in liquid nitrogen and finely ground in a coffee mill. After extraction with diethyl ether in a Soxhlet apparatus for 8 h, the extract was concentrated to ∼100 mL, and the volatiles were isolated by SAFE distillation (*17*). The distillate was separated into a neutral basic fraction and an acidic fraction by treatment with aqueous sodium carbonate to obtain the neutral/basic volatiles (NBF) and the acidic volatiles (AF). Both fractions were concentrated by means of a Vigreux column and a microdistillation apparatus to 250 μL for GC−olfactometry (*10*).

For roasting, ground, raw hazelnuts were thermally treated in a Teflon-coated pan held at 200 °C for 9−12 min until the characteristic aroma of roasted hazelnuts was perceivable. Extraction was performed as reported above for the raw nuts.

High-Resolution Gas Chromatography−Olfactometry (HRGC-O). HRGC-O was performed by means of a Carlo Erba gas chromatograph (type Mega 5160) using the capillaries DB-5 (30 m × 0.32 mm fused silica capillary) and FFAP (30 m × 0.32 mm fused silica capillary) (both J&W Scientific, Folsom, CA). The sample was applied by the cold-on-column injection technique at 40 °C, and the temperature of the oven was held isothermally for 2 min, then raised at 6 °C/min to 230 °C, and held isothermally for 5 min. For GC-O, the eluate was separated using a Y-type glass splitter; one part was led to a flame ionization detector (FID) and the other part to a heated sniffing port (200 °C). The sniffing port was used without humidified air, because the direct sniffing at the column outlet gave a more focused "odor puff". Retention data of the compounds were calculated as retention indices (RI) from the retention times of *n*-alkanes.

Aroma Extract Dilution Analysis. To determine the most odor-active compounds, an AEDA was carried out (*8*). For this purpose the aroma extract obtained was diluted 1:1 with the solvent-obtained dilutions with the factor of "2^n" (2, 4, 8, 16, 32, ...). The diluted extracts were analyzed by sniffing the effluent from the GC column, and the odor impressions were assigned. This process was repeated on all dilutions until no odor could be perceived. Each single odorant was, thus, assigned a flavor dilution (FD) factor of the last dilution in which the odor was perceived. The results are reported as a graph, with the abscissa corresponding to the retention index (RI) and the ordinate (exponential scale) to the FD factors. A comparative AEDA was carried out as described by Schieberle (*8*). Three experienced panelists performed the sensory analysis, and the data obtained were averaged.

High-Resolution Gas Chromatography−Mass Spectrometry (HRGC-MS). Mass spectrometric analyses were performed using a HRGC-MS system consisting of a HP 5890 series II gas chromatograph (Hewlett-Packard, Heilbronn, Germany) and an MAT 95 mass spectrometer (Finnigan, Bremen, Germany). Mass spectra in the electron impact mode (MS-EI) were generated at 70 eV and in the chemical ionization mode (MS-CI) at 115 eV using isobutane as the reactant gas.

Two-Dimensional Gas Chromatography−Mass Spectrometry. Aroma compounds were analyzed by means of two-dimensional gas chromatography−mass spectrometry, if coelution was observed. For this purpose, the volatiles were first separated on an FFAP column using a Mega 2 series gas chromatograph (Fisons Instruments, Mainz-Kastel, Germany). The compound of interest was cut out from the effluent using the MCSS-System (Moving Column Stream Switching-System) (Fisons Instruments) and was transferred via a cold trap into a second gas chromatograph (5160 Mega series, Carlo Erba, Hofheim, Germany) housing an OV-1701 or a DB-5 capillary (30 m × 0.32 mm, DB-5, 5 μm; J&W Scientific), respectively. The effluent was finally transferred into an ion trap detector (ITD 800) (Finnigan), and mass spectra were generated in MS-EI or MS-CI, respectively.

Proton Magnetic Resonance Spectra. ^{1}H NMR spectra were recorded in deuterated diethyl ether by means of a Bruker AMX 200 spectrometer operating at 400 MHz (Bruker, Karlsruhe, Germany). Trimethylsilane was used as the internal standard. The spectra were evaluated using the XWIN-NMR 3.1 program supplied by Bruker.

Sensory Evaluation. The overall sensory evaluation of the nut material was performed by aroma profile analysis using a sensory panel as previously described in more detail (*18*). A total of 12 expert panelists

recruited from the staff of the Institute was used and was trained as described in ref *18*.

RESULTS AND DISCUSSION

The raw hazelnuts and the roasted hazelnut material were both sensorially evaluated by a sensory panel using odor descriptors selected in preliminary sessions on the basis of the odors elicited by aqueous solutions of reference odorants in concentrations 100-fold above their odor thresholds. Although hazelnuts contain mainly fat, the matrix did not change the odor note of the reference compound.

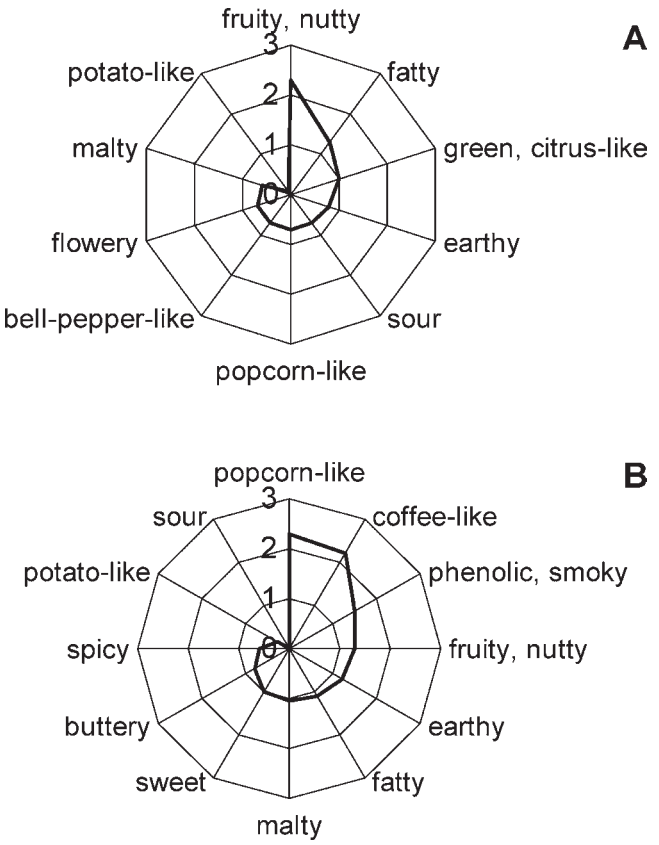

Figure 2. Aroma profiles of raw ground (**A**) and roasted ground hazelnut meal (**B**).

In the aroma profile of the raw nuts, an intense fruity−nutty aroma predominated, followed by fatty and green attributes (**Figure 2A**). In the roasted nut material, however, popcorn-like, coffee-like, and sweet−smoky aroma attributes predominated, whereas the fruity, nutty and fatty odor was not increased as compared to the raw nuts (**Figure 2B**).

Identification of Odor-Active Compounds in Raw Hazelnuts. To locate the odor-active compounds, the distillate obtained by a SAFE distillation of the extract from the raw hazelnuts was separated into NBF and the AF volatiles. In the NBF, a total of 37 odor-active volatiles was detected in the FD factor range of 4−4096 (**Figure 3**). The highest FD factors were determined for six odorants, namely, **21**, eliciting an intense bell pepper-like odor; followed by **9**, with a fruity hazelnut-like aroma; **18**, showing an earthy odor; **6**, with a fruity note; **13**, with a fruity, hazelnut-like aroma; and **30**, with a bell pepper-like attribute. By comparison of the retention indices on two stationary phases as well as the odor quality and the odor potency (peak area vs FD factor) with data available in an in-house database, structures were suggested for five of the six odorants. By comparison of the mass spectra (MS-EI; MS-CI) of the analytes with those of the respective reference compounds, the following identifications could successfully be performed: compound **21** was identified as the earthy-smelling 2-methoxy-3-isopropylpyrazine, **6** as ethyl 2-methylbutanoate, **13** as 5-methyl-(*E*)-2-hepten-4-one, **18** as 2-methoxy-3,5-dimethylpyrazine, and **30** as 2-methoxy-3-isobutylpyrazine (**Figure 4**).

However, for the mass spectrum obtained during elution of compound **9** (**Figure 5A**), no mass spectrum could be found in the literature. A comparison with the mass spectrum of **13** (**Figure 5B**) indicated that the base peak (*m*/*z* 71) and the molecular ion (MS-CI; data not shown) were both 2 units higher, suggesting that the odor detected with the elution of **9** could be referred to

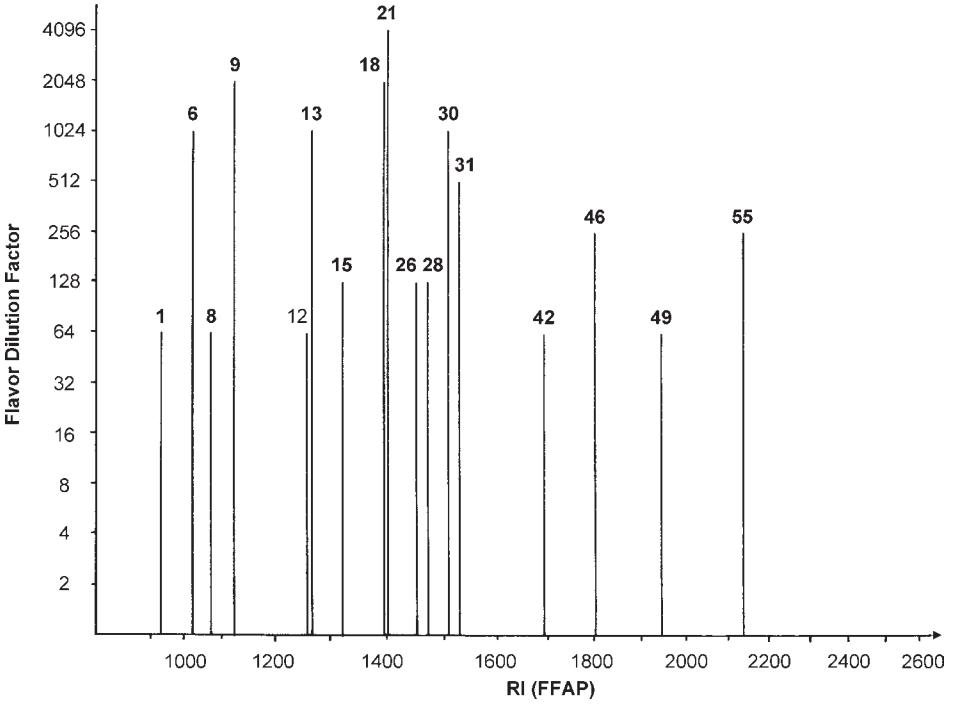

Figure 3. Flavor dilution chromatogram of the most odor-active neutral/basic odorants in raw hazelnuts (FD ≥ 64). Numbers correspond to those in **Table 1**.

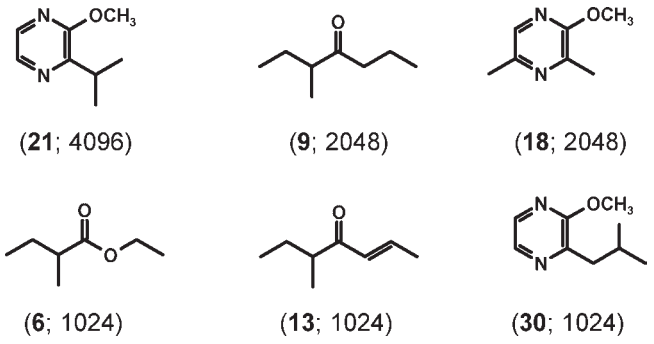

Figure 4. Structures of the key aroma compounds identified in raw hazelnuts (FD factor).

5-methyl-4-heptanone (**9**; **Figure 4**). Because this compound was commercially not available, it was synthesized by a new approach as detailed under Materials and Methods. The mass spectrometric data as well as the retention indices on two stationary phases and also the odor quality and the odor threshold of **9** were in full agreement with the data obtained for the reference compound 5-methyl-4-heptanone. The odor threshold of the saturated ketone in air (1.8 ng/L) was slightly higher as compared to the odor threshold of 5-methyl-(*E*)-2-hepten-4-one (0.08 ng/L). However, in water, both compounds showed the very low threshold of 0.05 μg/L, and both exhibited a similar fruity, hazelnut-like odor. Among the six key odorants identified in this study, previously only the 5-methyl-(*E*)-2-hepten-4-one (**13**; **Figure 4**) has been reported as a volatile constituent of raw hazelnuts (*2*, *3*).

High FD factors were also shown by the odor-active compounds **31**, **46**, and **55**, which, on the basis of reference odorants, were subsequently identified as linalool, (*E*)-β-damascenone, and 4-methylphenol (**Table 1**). In the AF, acetic acid (**25**), 2- and 3-methylbutanoic acid (sweaty; **39**), the isomers of which could not be separated on the FFAP column, and 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone (caramel-like; **56**) were identified, however, with somewhat lower FD factors.

The data confirmed 5-methyl-(*E*)-2-hepten-4-one (**13**) as a character impact odorant of hazelnuts as previously reported (*2*). However, the results indicated that additionally the saturated homologue 5-methyl-4-heptanone (**9**) contributes significantly to the aroma of the raw nuts. Both ketones are obviously generated during fruit ripening; however, although some suggestions have already been made for filbertone (*3*), the pathway of their biochemical formation is still open.

Also, the occurrence of the four earthy, peppery-smelling 2-methoxypyrazines (**18**, **21**, **28** and **30**) has so far not been reported in raw hazelnuts. 2-Methoxy-3-isopropyl- and 2-methoxy-3-isobutylpyrazine have also been identified in several plant materials (*19*); however, although a formation pathway from the respective parent amino acids and α-dicarbonyl compounds has been proposed, that is, 2-methoxy-3-isopropylpyrazine should be formed from L-valine or 2-methoxy-3-isobutylpyrazine from L-leucine, their biosynthetic pathway is still not established, that is, by labeling studies.

2-Methoxy-3,5-dimethylpyrazine (**18**; **Figure 4**) was previously reported also in green coffee beans (*16*) and is possibly formed by bacterial fermentation.

Characterization of Key Odorants in Ground Roasted Hazelnuts. Because the aroma compounds generated during roasting should be isolated from the freshly roasted material as quickly as possible, a model pan-roasting method was applied. The roasted hazelnut material obtained elicited an intense, typical roasted hazelnut-like aroma and was immediately used for volatile isolation. Although this procedure differs from the commercial roasting process, which is done on whole nuts, this procedure offered the possibility to have freshly roasted material always available for identification and quantification purposes. Although the concentrations of the odorants might differ from those in commercially roasted nuts, the overall aroma of the material was very similar to that of commercially roasted ground hazelnuts (data not shown).

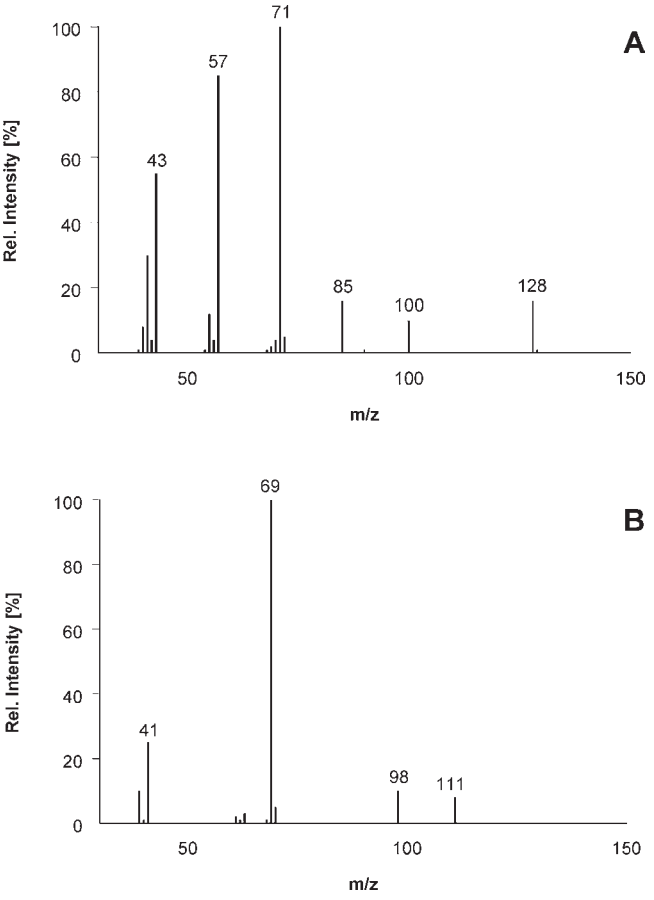

Figure 5. Mass spectra (MS-EI) obtained for compounds **9** (**A**) and **13** (**B**; 5-methyl-(*E*)-2-hepten-4-one).

Application of the AEDA on the distillate of the NBF resulted in the detection of 46 odor-active areas in the FD factor-range of 16−4096 (**Table 2**). The highest odor activities (FD factors) were found for **13** (fruity, hazelnut-like) as well as for **15** and **22**, both with popcorn-like odors. In an isolate from ~1 kg of the roasted material, the three odorants could be identified as 5-methyl-(*E*)-2-hepten-4-one (**13**), 2-acetyl-1-pyrroline (**15**), and 2-propionyl-1-pyrroline (**22**; **Figure 6**).

Somewhat lower FD factors were displayed by **19**, **29**, and **35**, each eliciting a fatty, waxy odor. The mass spectra obtained for these three compounds suggested their structures to be homologues of 2-alkenals. By comparing their analytical as well as the sensory data with those of the respective reference compounds, their structures could be assigned as (*Z*)-2-octenal (**19**), (*Z*)-2-nonenal (**29**), and (*Z*)-2-decenal (**35**; **Figure 6**). GC-O evaluation of the reference odorants confirmed that the three aldehydes were responsible for the fatty odors detected during GC-O of the distillate from the roasted nut material.

High FD factors were also displayed by **6** (fruity), **9** (fruity, hazelnut-like), **41** (coffee-like, sulfury), and **45** (deep-fried) (**Table 2**). Among them, on the basis of the available reference compounds, **6** could be identified as ethyl 2-methylbutanoate, **9** as 5-methyl-4-heptanone, and **45** as (*E*,*E*)-2,4-decadienal (**Figure 6**).

Table 1. Key Aroma Compounds (FD ≥ 4) Identified in Raw Hazelnuts

no.	odorant[a]	odor quality[b]	RI on FFAP	RI on DB-5	FD factor[c]
1	3-methylbutanal	malty	940	655	64
2	2-methylbutanal	malty	961	664	4
3	ethyl propanoate	fruity	970	724	4
4	α-pinene	terpene-like	1000	939	4
6	ethyl 2-methylbutanoate	fruity	1034	846	1024
8	hexanal	green	1062	795	64
9	5-methyl-4-heptanone	fruity, hazelnut-like	1129	920	2048
12	octanal	fatty, green	1263	1003	64
13	5-methyl-(*E*)-2-hepten-4-one	fruity, hazelnut-like	1267	972	1024
14	1-octen-3-one	mushroom-like	1282	975	32
15	2-acetyl-1-pyrroline	popcorn-like	1326	913	128
17	nonanal	fatty, green	1339	1105	4
18	2-methoxy-3,5-dimethylpyrazine	earthy	1391	1054	2048
21	2-methoxy-3-isopropylpyrazine	green, bell pepper-like	1400	1086	4096
25	acetic acid[d]	sour	1436	nd	128
26	3-(methylthio)propanal	cooked, potato-like	1441	907	128
28	2-methoxy-3-*sec*-butylpyrazine	bell pepper-like	1472	1176	128
29	(*Z*)-2-nonenal	fatty	1490	1150	32
30	2-methoxy-3-isobutylpyrazine	bell pepper-like	1509	1184	1024
31	linalool	flowery	1521	1103	512
32	2-methylpropanoic acid[d]	sweaty	1547	nd	4
34	(*E*,*Z*)-2,6-nonadienal	cucumber-like	1571	1152	4
35	(*Z*)-2-decenal	fatty	1590	1247	16
36	butanoic acid[d]	sweaty	1612	nd	4
37	phenylacetaldehyde	flowery, honey-like	1632	1047	16
38	(*E*)-2-decenal	fatty	1641	1255	4
39	2- and 3-methylbutanoic acid[d]	sweaty	1645	nd	64
42	(*E*,*E*)-2,4-nonadienal	fatty	1692	1219	64
46	(*E*)-β-damascenone	boiled apple-like	1801	1388	256
47	2-methoxyphenol[d]	phenolic, smoky	1860	1095	32
48	2,4,6-nonatrienal	oats-like	1883	1270	4
49	2-phenylethanol	flowery, honey-like	1940	1117	64
50	γ-octalactone	coconut-like	1979	1264	8
51	*trans*-4,5-epoxy-(*E*)-2-decenal	metallic	2018	1388	32
54	γ-nonalactone	coconut-like	2063	1363	32
55	4-methylphenol	horse-like	2071	1080	256
56	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone[d]	caramel	2079	nd	64

[a] The compound was identified by comparison with the reference substance on the basis of the following criteria: RI on the two stationary phases given in the table, mass spectra obtained by MS-EI and MS-CI, and odor qualitiy perceived at the sniffing port. [b] Odor description assigned during AEDA. [c] Flavor dilution (FD) factor determined during AEDA. [d] Compound was identified in the fraction containing the acidic volatiles.

For the mass spectrum of compound **41** (**Figure 7A**), however, no comparable mass spectrum could be found in the literature on food aroma compounds, but the compound showed a similar coffee-like odor quality as 2-furfurylthiol (**23**) (**Table 2**). Because the base peak *m*/*z* 97 and the molecular ion *m*/*z* 130 of **41** were exactly 16 mass units higher than those of 2-furfurylthiol (**Figure 7B**), the structure of **41** was suggested to be 2-thienylthiol. A comparison of the analytical data as well as the sensory attributes with the reference compound showed a very good agreement with data obtained for **41**. Thus, this odorant was identified as 2-thienylthiol, showing odor thresholds in air of 0.5 ng/L and in water of 0.6 μg/L.

The fraction containing the acidic odorants elicited an intense coffee- and caramel-like odor, and the application of the AEDA revealed six odorants in the FD factor range of 64−2048 (**23**, **25**, **36**, **47**, **53**, **57**). The highest FD factor was shown by compound **47**, eliciting a phenolic odor. Identification experiments revealed its structure as 2-methoxyphenol. Furthermore, 2-furfurylthiol (**23**), 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**53**), acetic acid (**25**), and butanoic acid (**36**) could readily be identified as additional odorants in the AF.

However, the mass spectrum obtained for compound **57** (**Figure 8A**), eliciting an intense seasoning-like odor identical to that of 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (3-HDF), was not available in the literature. A comparison with the mass spectrum of 3-HDF (**Figure 8B**) also suggested a 2-furanone structure for **57** due to the intense *m*/*z* 83 fragment. Because the molecular ion of **57** (*m*/*z* 126) was 2 mass units lower than that of 3-HDF (*m*/*z* 128), a trimethyl-substituted 2(5*H*)-furanone could be derived from the mass spectrometric data. Thus, two possibilities should exist for a structural proposal: (i) 3,4,5-trimethyl-2(5*H*)-furanone or (ii) 3,5,5′-trimethyl-2(5*H*)-furanone. Because both compounds were commercially not available, a route for the preparation of the latter furanone was developed first as shown in **Figure 1**. The suggested reaction pathway led to the successful synthesis of 3,5,5′-trimethyl-2(5*H*) furanone, the structure of which was confirmed by NMR. Because its mass spectra (MS-EI; MS-CI) as well as the retention indices, odor quality, and odor threshold agreed with the data obtained for **57**, the odorant was identified as 3,5,5′-trimethyl-2(5*H*)-furanone. This is the first report of this compound as a food odorant.

A comparison of the key odorants in the raw nuts and the roasted materials on the basis of their FD factors revealed that quite a high number of important odorants in the roasted nuts were sensorially not detectable or detectable with only a low FD factor, respectively, in the raw nuts (**Table 3**), for example, the

Table 2. Key Aroma Compounds (FD ≥ 16) Identified in the Roasted Hazelnut Paste

no.	odorant[a]	odor quality[b]	RI on FFAP	RI on DB-5	FD factor
1	3-methylbutanal	malty	940	652	256
2	2-methylbutanal	malty	961	654	16
5	2,3-butandione	buttery	967	<600	16
6	ethyl 2-methylbutanoate	fruity	1028	851	1024
7	2,3-pentandione	buttery	1049	704	128
8	hexanal	green	1075	800	32
9	5-methyl-4-heptanone	fruity, hazelnut-like	1129	921	1024
10	(*Z*)-5-methyl-2-hepten-4-one	fruity, hazelnut-like	1192	905	256
11	(*Z*)-4-heptenal	rotten	1230	903	16
12	octanal	fatty, green	1257	1003	512
13	5-methyl-(*E*)-2-hepten-4-one	fruity, hazelnut-like	1263	975	4096
14	1-octen-3-one	mushroom-like	1277	978	64
15	2-acetyl-1-pyrroline	popcorn-like	1318	925	4096
16	dimethyl trisulfide	sulfur-like, cabbage-like	1329	966	256
17	nonanal	fatty, green	1343	1105	16
19	(*Z*)-2-octenal	fatty	1393	1048	2048
20	2,3,5-trimethylpyrazine	earthy	1399	1000	256
22	2-propionyl-1-pyrroline	popcorn-like	1400	1025	2048
23	2-furfurylthiol[c]	coffee-like	1400	nd	2048
24	(*E*)-2-octenal	fatty, green	1409	1059	16
25	acetic acid[c]	sour	1427	nd	256
26	3-(methylthio)propanal	potato-like	1441	910	512
27	2-ethyl-3,5-dimethylpyrazine	earthy	1447	1093	512
29	(*Z*)-2-nonenal	fatty	1490	1146	2048
30	2-isobutyl-3-methoxypyrazine	bell pepper-like	1509	1184	64
31	linalool	flowery	1521	1103	64
32	(*E*)-2-nonenal	fatty, green	1533	1157	64
33	unknown	phenolic	1560	nd	256
34	(*E*,*Z*)-2,6-nonadienal	cucumber-like	1571	1152	16
35	(*Z*)-2-decenal	fatty	1585	1255	2048
36	butanoic acid[c]	sweaty	1607	nd	64
37	(*E*)-2-decenal	fatty	1610	1268	16
38	phenylacetaldehyde	honey-like	1632	1047	128
40	(*E*,*Z*)-2,4-nonadienal	fatty	1658	1194	16
41	2-thienylthiol	coffee-like	1685	1093	1024
42	(*E*,*E*)-2,4-nonadienal	fatty	1695	1202	256
43	(*E*,*Z*)-2,4-decadienal	deep-fried	1749	1300	256
44	γ-heptalactone	peach-like	1798	1184	256
45	(*E*,*E*)-2,4-decadienal	fatty	1800	1324	1024
46	(*E*)-β-damascenone	boiled apple-like	1801	1388	128
47	2-methoxyphenol[c]	phenolic, smoky	1860	1095	1024
49	2-phenylethanol	honey-like	1940	1117	64
51	*trans*-4,5-epoxy-(*E*)-2-decenal	metallic	2018	1386	512
52	4-methoxybenzaldehyde	anise-like	2030	1265	32
53	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone[c]	sweet	2053	nd	512
57	3,5,5-trimethyl-2(5*H*)-furanone[c]	spicy	2234	nd	256

[a] The compound was identified by comparing it with the reference substance on basis of the following criteria: RI on the two stationary phases given in the table, mass spectra obtained by MS-EI and MS-CI and odor qualitiy perceived at the sniffing port. [b] Odor description assigned during AEDA. [c] The compound was identified in the acidic fraction.

popcorn-like-smelling odorants 2-acetyl-1-pyrroline and 2-propionyl-1-pyrroline, as well as the coffee-like, sulfury-smelling thiols 2-furfurylthiol and 2-thenylthiol. This comparison was possible because the same amount of both nut materials was extracted, the distillates were concentrated to the same volume (250 μL), and the same volume (1 μL) was injected onto the GC column in this approach assigned as comparative AEDA (*8*).

2-Acetyl-1-pyrroline and 2-propionyl-1-pyrroline have previously been identified as degradation products of proline in the presence of reducing carbohydrates (*20*), whereas 2-furfurylthiol and 2-thienylthiol were characterized as degradation products in cysteine−hexose reactions (*21*). It can, thus, be concluded that these odorants are formed during roasting of the hazelnut paste by a degradation of these free amino acids occurring in the raw nuts.

The occurrence of the (*Z*)-alkenals, (*Z*)-2-octenal, (*Z*)-2-nonenal, and (*Z*)-2-decenal, with such high FD factors, has not been reported before in studies on food aromas. However, because these compounds are known degradation products of lipid hydroperoxides, it might be assumed that the odorants are generated from unsaturated fatty acids during pan-roasting. However, although grinding before roasting increases the possibility of a reaction of the unsaturated fatty acids with oxygen, it is quite surprising that predominantly the (*Z*)-aldehydes are formed. Furthermore, when radical-induced lipid degradation mechanisms were applied on oleic acid, the main fatty acid in hazelnut oil, only the formation of (*Z*)-2-decenal can easily be explained by a degradation of the respective 9-hydroperoxide. Thus, the data suggest a different mechanism in the formation of, for example, (*Z*)-2-octenal.

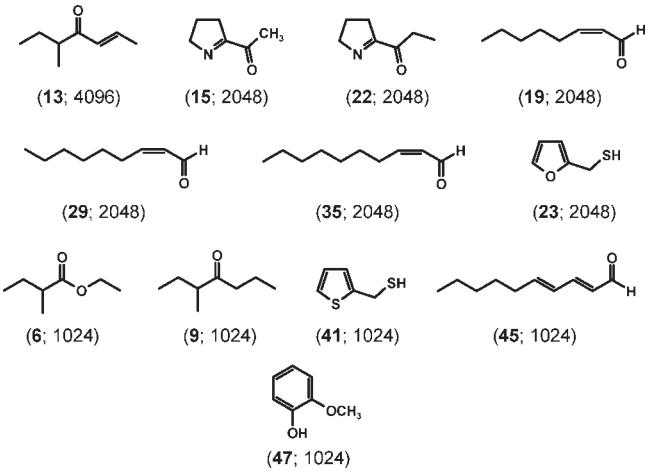

Figure 6. Structures of the key odorants identified in the roasted hazelnut meal.

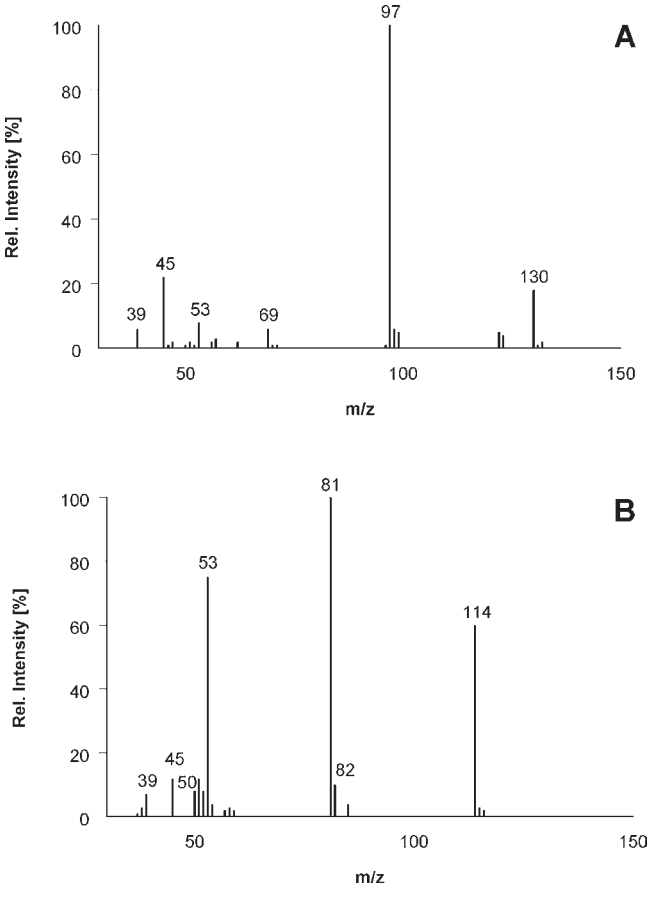

Figure 7. Mass spectrum obtained for compound **41** (**A**) and for 2-furfurylthiol (**B**).

The increase in 2-methoxyphenol during roasting (**Table 3**) might be explained by a decarboxylation from its precursor vanillic acid during the thermal treatment as previously shown in a model experiment (*22*). However, the presence of vanillic acid in hazelnuts has not yet been reported.

5-Methyl-(*E*)-2-hepten-4-one (**13**) was also increased during roasting, but already showed a quite high FD factor in the raw hazelnuts (**Tables 1** and **2**). The ketone was previously suggested to be biochemically formed in the hazelnuts (*3*), but an increase upon roasting was later observed by us (*23*) and also confirmed by another group (*7*). Because in the roasted hazelnuts also the

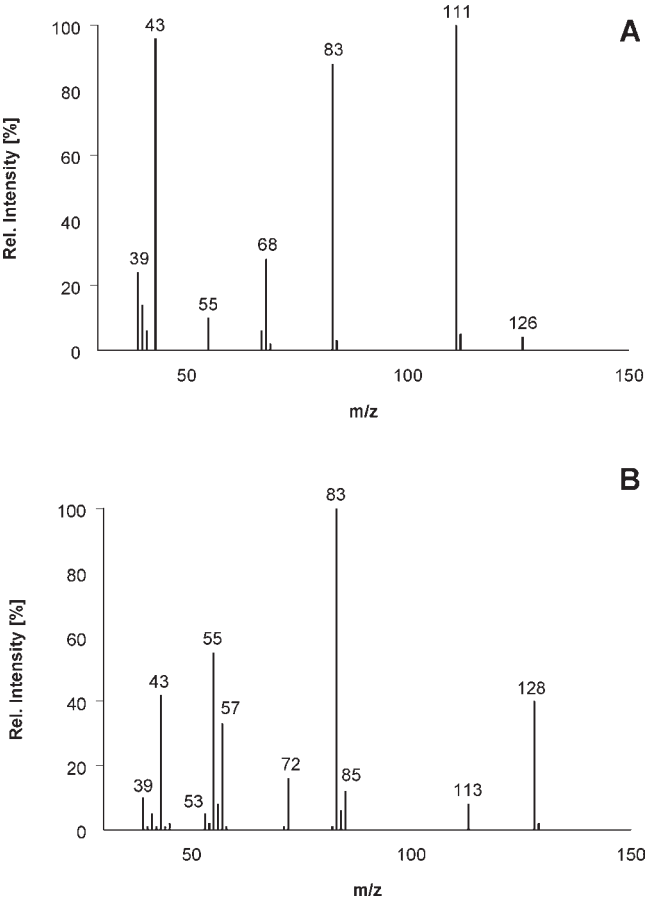

Figure 8. Mass spectrum obtained for compound **57** (**A**) and for 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (**B**).

Table 3. Comparison of the Flavor Dilution Factors of Key Odorants in Extracts from Raw Hazelnuts (UHN) and Roasted Hazelnut Paste (RHN) by a Comparative Aroma Extract Dilution Analysis (*8*)

		FD in	
odorant	odor quality	RHN	UHN
2-acetyl-1-pyrroline	popcorn-like	4096	128
2-propionyl-1-pyrroline	popcorn-like	2048	<1
2-furfurylthiol	coffee-like, sulfury	2048	<1
2-thenylthiol	coffee-like, sulfury	1024	<1
(*Z*)-2-octenal	fatty, waxy	2048	<1
(*Z*)-2-decenal	fatty, waxy	2048	<1
(*Z*)-2-nonenal	fatty, waxy	2048	32
2-methoxyphenol	sweet, phenolic	1024	32
(*E*,*E*)-2,4-decadienal	deep-fried	1024	2
3,5,5′-trimethyl-2(5*H*)-furanone	seasoning-like	256	<1
2-ethyl-3,5-dimethylpyrazine	roasty, potato	512	<1
dimethyl trisulfide	cabbage-like	256	<1
2,3,5-trimethylpyrazine	roasty, potato	256	<1
2,3-pentandione	buttery	128	<1

(*Z*)-isomer of 5-methyl-(*E*)-2-hepten-4-one was detected among the key odorants (**10**; **Table 2**), this is another hint at the formation of both isomers from yet unknown precursors during the thermal treatment.

The results presented here show that the application of GC-O on unroasted and roasted seeds from the same batch is a powerful tool to differentiate between those key aroma compounds of a food product which are already present in the raw material and others which are generated from odorless precursors during thermal processing. Thus, a selection of raw materials for certain

applications can be done on the basis of, for example, a quantitative analysis of specific aroma precursors. This information can, for example, be used by plant breeders.

To confirm the data obtained, quantitative studies and aroma recombination experiments are underway.

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